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Electrolysis of water

(Redirected from Water electrolysis)

Electrolysis of water is using electricity to <u>split water</u> into $\underline{oxygen}(O_2)$ and <u>hydrogen</u> (H₂) gas by <u>electrolysis</u>. Hydrogen gas released in this way can be used as <u>hydrogen fuel</u>, or remixed with the <u>oxygen</u> to create <u>oxyhydrogen</u> gas, for use in <u>welding</u> and other applications.

Water electrolysis requires a minimum potential difference of 1.23 volts, although at that voltage external heat is also required. Typically 1.5 volts are provided. Electrolysis is rare in industrial applications since hydrogen can be produced less expensively from fossil fuels.^[1]

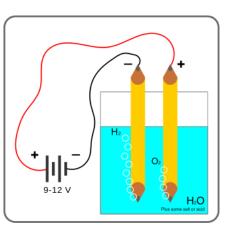
History

In 1789, Jan Rudolph Deiman and Adriaan Paets van Troostwijk used an electrostatic machine to make electricity that was discharged on gold electrodes in a Leyden jar.^[2] In 1800 Alessandro Volta invented the voltaic pile, while a few weeks later English scientists William Nicholson and Anthony Carlisle used it to electrolyse water. In 1806 Humphry Davy reported the results of extensive distilled water electrolysis experiments, concluding that <u>nitric acid</u> was produced at the anode from dissolved atmospheric nitrogen. He used a high voltage battery and nonreactive electrodes and vessels such as gold electrode cones that doubled as vessels bridged by damp asbestos.^[3] Zénobe Gramme invented the Gramme machine in 1869, making electrolysis a cheap method for hydrogen production. A method of industrial synthesis of hydrogen and oxygen through electrolysis was developed by Dmitry Lachinov in 1888.^[4]

Principles

A DC electrical power source is connected to two electrodes, or

two plates (typically made from an inert metal such as platinum or iridium) that are placed in the water. Hydrogen appears at the <u>cathode</u> (where <u>electrons</u> enter the water), and oxygen at the <u>anode.^[5]</u> Assuming ideal faradaic efficiency, the <u>amount</u> of hydrogen generated is twice the amount of oxygen, and both are proportional to the total <u>electrical charge</u> conducted by the solution.^[6] However, in many cells <u>competing side reactions</u> occur, resulting in additional products and less than ideal faradaic efficiency.



Simple setup for demonstration of electrolysis of water at home



An <u>AA battery</u> in a glass of <u>tap water</u> with <u>salt</u> showing <u>hydrogen</u> produced at the negative terminal

<u>Electrolysis</u> of pure water requires excess energy in the form of <u>overpotential</u> to overcome various activation barriers. Without the excess energy, electrolysis occurs slowly or not at all. This is in part due to the limited <u>self-ionization of water</u>.

Pure water has an <u>electrical conductivity</u> about one-millionth that of seawater.

Many <u>electrolytic cells</u> lack requisite <u>electrocatalysts</u>. Efficiency is increased through the addition of an <u>electrolyte</u> (such as a <u>salt</u>, an <u>acid</u> or a <u>base</u>) and <u>electrocatalysts</u>.

Equations

In pure water at the negatively charged cathode, a <u>reduction</u> reaction takes place, with electrons (e⁻) from the cathode given to hydrogen cations to form hydrogen gas. The <u>half reactions</u>, balanced with acid, are:

Cathode (reduction): 2 H₂O(l) + 2e⁻ \rightarrow H₂(g) + 2 OH⁻(aq) Anode (oxidation): 2 OH⁻(aq) \rightarrow 1/2 O₂(g) + H₂O(l) + 2 e⁻

 $2H_2O \longrightarrow 2H_2 + O_2$

Diagram showing the overall chemical equation.

water

Reduction at cathode

 $2\mathrm{H}^{+}(\underline{aq}) + 2\mathrm{e}^{-} \rightarrow \mathrm{H}_{2}(\underline{g})$

At the positively charged anode, an <u>oxidation</u> reaction occurs, generating oxygen gas and giving electrons to the anode to complete the circuit:

Oxidation at anode

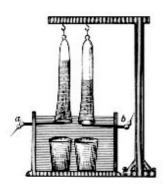
 $2 \text{ H}_2\text{O}(\underline{\textbf{/}}) \rightarrow \text{O}_2(g) + 4 \text{ H}^+(aq) + 4\text{e}^-$

The same half-reactions can be balanced with the base as listed below. Not all half-reactions must be balanced with acid or base. Many do, like the listed oxidation or reduction of water. Half reactions must be balanced with either acid or base. Acid-balanced reactions predominate in acidic (low pH) solutions, while base-balanced reactions predominate in basic (high pH) solutions.

Combining either half reaction pair yields the same overall decomposition of water into oxygen and hydrogen:

Overall reaction: $2 H_2O(h) \rightarrow 2 H_2(g) + O_2(g)$

The number of hydrogen molecules produced is twice the number of oxygen molecules. Assuming equal temperature and pressure for both gases, the produced hydrogen gas has, therefore, twice the volume of the produced oxygen gas. The number of electrons pushed through the water is twice the number of generated hydrogen molecules and four times the number of generated oxygen molecules.



Device invented by Johann Wilhelm Ritter to

develop the electrolysis of

Thermodynamics

The decomposition of pure water into hydrogen and oxygen at <u>standard temperature and pressure</u> is not favorable in thermodynamic terms.

Anode (oxidation): $\begin{array}{c} 2\\H_2O(I)\end{array} \rightarrow \begin{array}{c} O_2(g) + 4\\H^+(aq) +\\4e^-\end{array} \qquad \begin{array}{c} E^o = +1.23 \text{ V}\\(\text{for the}\\reduction \text{ half-}\\equation)\end{array}$ Cathode (reduction): $\begin{array}{c} 2\\H^+(aq)\\+2e^-\end{array} \rightarrow H_2(g) \qquad E^o = 0.00 \text{ V}\end{array}$

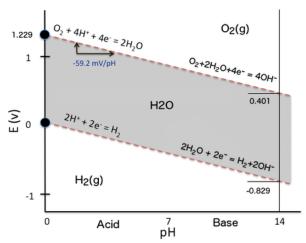
Thus, the standard potential of the water electrolysis cell ($E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$) is -1.229 V at 25 °C at pH o ([H⁺] = 1.0 M). At 25 °C with pH 7 ([H⁺] = 1.0 × 10⁻⁷ M), the potential is unchanged based on the Nernst equation. The thermodynamic standard cell potential can be obtained from standard-state free energy calculations to find ΔG^{o} and then using the equation: $\Delta G^{o} = -n$ F E^o (where E^o is the cell potential and F the Faraday constant, i.e. 96,485.3321233 C/mol). For two water molecules electrolysed and hence two hydrogen molecules formed, n = 4, and

- ∆G° = 474.48 kJ/2 mol(water) = 237.24 kJ/mol(water)
- $\Delta S^{\circ} = 163 \text{ J/K mol(water)}$
- ΔH° = 571.66 kJ/2 mol(water) = 285.83 kJ/mol(water)
- and 141.86 kJ/g(H₂).

However, calculations regarding individual electrode equilibrium potentials requires corrections to account for the activity coefficients.^[7] In practice when an electrochemical cell is "driven" toward completion by applying reasonable potential, it is kinetically controlled. Therefore, <u>activation energy</u>, ion mobility (diffusion) and concentration, wire resistance, surface hindrance including bubble formation (blocks electrode area), and entropy, require greater potential to overcome. The amount of increase in required potential is termed the overpotential.

Electrolyte

Electrolysis in pure water consumes/reduces H^+ <u>cations</u> at the cathode and consumes/oxidizes hydroxide (OH⁻) <u>anions</u> at the anode. This can be verified by adding a <u>pH</u> indicator to the water: Water near the cathode is basic while water near the anode is acidic. The hydroxides OH⁻ that approach the anode mostly combine with the positive hydronium ions (H₃O⁺) to form water. The positive hydronium ions that approach the cathode mostly combine with negative hydroxide ions to form water. Relatively few hydroniums/hydroxide ions reach the cathode/anode. This can cause overpotential at both electrodes.



Pourbaix diagram for water, including equilibrium regions for water, oxygen and hydrogen at STP. The vertical scale is the electrode potential of hydrogen or non-interacting electrode relative to an <u>SHE</u> electrode, the horizontal scale is the <u>pH</u> of the electrolyte (otherwise non-interacting). Neglecting <u>overpotential</u>, above the top line the equilibrium condition is oxygen gas, and oxygen will bubble off of the electrode until equilibrium is reached. Likewise, below the bottom line, the equilibrium condition is hydrogen gas, and hydrogen will bubble off of the electrode until equilibrium is reached.

Pure water has a charge carrier density similar to semiconductors^[8] since it has a low <u>autoionization</u>, $K_w = 1.0 \times 10^{-14}$ at room temperature and thus pure water conducts current poorly, 0.055 μ S·cm⁻¹.^[9] Unless a large potential is applied to increase the autoionization of water, electrolysis of pure water proceeds slowly, limited by the overall conductivity.

An aqueous electrolyte can considerably raise conductivity. The electrolyte disassociates into <u>cations</u> and anions; the anions rush towards the anode and neutralize the buildup of positively charged H^+ there; similarly, the cations rush towards the cathode and neutralize the buildup of negatively charged OH^- there. This allows the continuous flow of electricity.^[10]



Hoffman voltameter connected to a direct current power supply

Anions from the electrolyte compete with the hydroxide ions to give up an <u>electron</u>. An electrolyte anion with less <u>standard electrode potential</u> than hydroxide will be oxidized instead of the hydroxide, producing no oxygen gas. Likewise, a <u>cation</u> with a greater <u>standard electrode potential</u> than a hydrogen ion will be reduced instead of hydrogen.

Various <u>cations</u> have lower <u>electrode</u> potential than H⁺ and are therefore suitable for use as electrolyte cations: $\underline{\text{Li}}^+$, $\underline{\text{Rb}}^+$, $\underline{\overline{\text{K}}}^+$, $\underline{\text{Cs}}^+$, $\underline{\text{Ba}}^{2+}$, $\underline{\text{Sr}}^{2+}$, $\underline{\text{Ca}}^{2+}$, $\underline{\text{Na}}^+$, and $\underline{\text{Mg}}^{2+}$. <u>Sodium</u> and <u>lithium</u> are common choices, as they form inexpensive, soluble salts.

If an <u>acid</u> is used as the electrolyte, the cation is H^+ , and no competitor for the H^+ is created by disassociating water. The most commonly used anion is <u>sulfate</u> (SO₄²⁻), as it is difficult to oxidize. The standard potential for oxidation of this ion to the peroxydisulfate ion is +2.010 volts.[11]

Strong acids such as <u>sulfuric acid</u> (H_2SO_4), and strong bases such as <u>potassium hydroxide</u> (KOH), and <u>sodium hydroxide</u> (NaOH) are common choices as electrolytes due to their strong conducting abilities.

A solid polymer electrolyte can be used such as <u>Nafion</u> and when applied with an appropriate catalyst on each side of the membrane can efficiently electrolyze with as little as 1.5 volts. Several commercial electrolysis systems use solid electrolytes.^[12]

Pure water

Electrolyte-free pure water electrolysis has been achieved via deep-sub-Debye-length nanogap electrochemical cells. When the gap between cathode and anode are smaller than Debye-length (1 micron in pure water, around 220 nm in distilled water), the double layer regions from two electrodes can overlap, leading to a uniformly high electric field distributed across the entire gap. Such a high electric field can significantly enhance ion transport (mainly due to migration), further enhancing self-ionization, continuing the reaction and showing little resistance between the two electrodes. In this case, the two half-reactions are coupled and limited by electron-transfer steps (the electrolysis current is saturated at shorter electrode distances).^[13]

Seawater

Ambient seawater presents challenges because of the presence of salt and other impurities.

Approaches may or may not involve desalination before electrolysis. Traditional electrolysis produces toxic and corrosive chlorine ions (e.g., Cl⁻ and ClO⁻). Multiple methods have been advanced for electrolying unprocessed seawater. Typical proton exchange membrane (PEM) electrolysers require desalination.

Techniques

As of 2022, commercial electrolysis requires around 53 kWh of electricity to produce one kg of hydrogen, which holds 33.6 kWh of energy.^[14]

Fundamental demonstration

Two leads, running from the terminals of a battery, placed in a cup of water with a quantity of electrolyte establish conductivity. Using <u>NaCl</u> (salt) in an electrolyte solution yields <u>chlorine</u> gas rather than oxygen due to a <u>competing half-reaction</u>. <u>Sodium bicarbonate</u> (baking soda) instead yields hydrogen, and carbon dioxide for as long as the bicarbonate anion stays in solution.

Hofmann voltameter

The Hofmann voltameter is a small-scale electrolytic cell. It consists of three joined upright cylinders. The inner cylinder is open at the top to allow the addition of water and electrolyte. A <u>platinum</u> electrode (plate or honeycomb) is placed at the bottom of each of the two side cylinders, connected to the terminals of an electricity source. The generated gases displace water and collect at the top of the two outer tubes, where it can be drawn off with a stopcock.



Match test used to detect the presence of hydrogen gas

High-pressure

High-pressure electrolysis involves <u>compressed hydrogen</u> output around 12–20 MPa (120–200 <u>Bar</u>, 1740–2900 <u>psi</u>).^[15] By pressurising the hydrogen in the electrolyser, the need for an external hydrogen compressor is eliminated. The average energy consumption is around 3%.^[16]

High-temperature

High-temperature electrolysis (also HTE or steam electrolysis) is more efficient at higher temperatures. A heat engine supplies some of the energy, which is typically cheaper than electricity [17][18]

Alkaline water electrolysis

<u>Alkaline water electrolysis</u> is a type of <u>electrolyzer</u> that is characterized by having two <u>electrodes</u> operating in a liquid alkaline electrolyte solution of <u>potassium hydroxide</u> (KOH) or <u>sodium hydroxide</u> (NaOH). These electrodes are separated by a diaphragm, separating the product gases and

transporting the hydroxide ions (OH⁻) from one electrode to the other. [19][20] A recent comparison showed that state-of-the-art nickel based water electrolyzers with alkaline electrolytes lead to competitive or even better efficiencies than acidic polymer electrolyte membrane water electrolysis with platinum group metal based electrocatalysts. [21]

The technology has a long history in the chemical industry. The first large-scale demand for hydrogen emerged in late 19th century for <u>lighter-than-air aircraft</u>, and before the advent of <u>steam reforming</u> in the 1930s, the technique was competitive.

Proton exchange membrane

A <u>proton-exchange membrane electrolyser</u> separates reactants and transports protons while blocking a direct electronic pathway through the membrane. PEM fuel cells use a solid polymer membrane (a thin plastic film) which is permeable to hydrogen ions (<u>protons</u>) when it is saturated with water, but does not conduct electrons.

It uses a proton-exchange membrane, or polymer-electrolyte membrane (PEM), which is a <u>semipermeable membrane</u> generally made from <u>ionomers</u> and designed to <u>conduct protons</u> while acting as an insulator and reactant barrier, e.g. to <u>oxygen</u> and <u>hydrogen</u> gas.^[22] PEM fuel cells use a solid polymer membrane (a thin plastic film) that is permeable to protons when saturated with water, but does not conduct electrons. Proton-exchange membranes are primarily characterized by proton conductivity (σ), methanol permeability (*P*), and thermal stability.^[23]

PEMs can be made from either pure polymer or from <u>composite</u> membranes, where other materials are embedded in a polymer matrix. One of the most common commercially available materials is the <u>fluoropolymer</u> (PFSA)^[24] <u>Nafion</u>.^[25] Nafion is an ionomer with a <u>perfluorinated</u> backbone such as <u>Teflon</u>.^[26] Many other structural motifs are used to make ionomers for proton-exchange membranes. Many use polyaromatic polymers, while others use partially fluorinated polymers.

Supercritical water

Supercritical water electrolysis (SWE) uses water in a supercritical state. Supercritical water requires less energy, therefore reducing costs. It operates at >375 °C, which reduces thermodynamic barriers and increases kinetics, improving ionic conductivity over liquid or gaseous water, which reduces ohmic losses. Benefits include improved electrical efficiency, >221bar pressurised delivery of product gases, ability to operate at high current densities and low dependence on precious metal catalysts. As of 2021 commercial SWE equipment was not available.^[27]

Nickel/iron

In 2014, researchers announced electrolysis using nickel and iron catalysts rather than precious metals. Nickel-metal/nickel-oxide structure is more active than nickel metal or nickel oxide alone. The catalyst significantly lowers the required voltage.^{[28][29]} Nickel-iron batteries are under investigation for use as combined batteries and electrolysers. Those "battolysers" could be charged and discharged like conventional batteries, and would produce hydrogen when fully charged.^[30]

In 2023, researchers in Austalia announced the use of a porous sheet of nitrogen-doped nickel molybdenum phosphide catalyst. The nitrogen doping increases conductivity and optimizes

electronic density and surface chemistry. This produces additional catalytic sites. The nitrogen bonds to the surface metals and has electro-negative properties that help exclude unwanted ions and molecules, while phosphate, sulfate, nitrate and hydroxyl surface ions block chlorine and prevent corrosion.10 mA cm-2 can be achieved using 1.52 and 1.55 V in alkaline electrolyte and <u>seawater</u>, respectively.^[31]

Nanogap electrochemical cells

In 2017, researchers reported nanogap <u>electrochemical cells</u> that achieved high-efficiency electrolytefree pure water electrolysis at ambient temperature. In these cells, the two electrodes are so close to each other (smaller than <u>Debye-length</u>) that the mass transport rate can be higher than the electrontransfer rate, leading to two <u>half-reactions</u> coupled together and limited by the electron-transfer step. Experiments show that the electrical current density can be larger than that from 1 mol/L sodium hydroxide solution. Its "Virtual Breakdown Mechanism", is completely different from traditional electrochemical theory, due to such nanogap size effects.^[13]

Capillary fed

A capillary-fed electrolyzer cell is claimed to require only 41.5 kWh to produce 1 kg of hydrogen. The water electrolyte is isolated from the electrodes by a porous, hydrophilic separator. The water is drawn into the electrolyzer by capillary action, while the electrolyzed gases pass out on either side. It extends PEM technology by eliminating bubbles that reduce the contact between the electrodes and the electrolyte, reducing efficiency. The design is claimed to operate at 98% energy efficiency. The design forgoes water circulation, separator tanks, and other mechanism and can be air- or radiatively cooled.^[14]

Applications

About five percent of hydrogen gas produced worldwide is created by electrolysis. The vast majority of current industrial hydrogen production is from <u>natural gas</u> in the <u>steam reforming</u> process, or from the partial oxidation of <u>coal</u> or heavy hydrocarbons. The majority of the hydrogen produced through electrolysis is a side product in the production of <u>chlorine</u> and <u>caustic soda</u>. This is a prime example of a competing for side reaction.

 $2NaCl + 2H_2O \rightarrow Cl_2 + H_2 + 2NaOH$

In the <u>chloralkali process</u> (electrolysis of brine) a water/sodium chloride mixture is only half the electrolysis of water since the <u>chloride</u> ions are oxidized to <u>chlorine</u> rather than water being oxidized to oxygen. Thermodynamically, this would not be expected since the oxidation potential of the chloride ion is less than that of water, but the rate of the chloride reaction is much greater than that of water, causing it to predominate. The hydrogen produced from this process is either burned (converting it back to water), used for the production of <u>specialty chemicals</u>, or various other small-scale applications.

Water electrolysis is also used to generate oxygen for the International Space Station. [32][33]

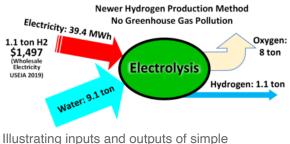
Many industrial electrolysis cells are similar to <u>Hofmann voltameters</u>, with platinum plates or honeycombs as electrodes. Generally, hydrogen is produced for point of use applications such as <u>oxyhydrogen</u> torches or when <u>high purity hydrogen</u> or oxygen is desired. The vast majority of hydrogen is produced from hydrocarbons and as a result, contains trace amounts of <u>carbon</u> <u>monoxide</u> among other impurities. The carbon monoxide impurity can be detrimental to various systems including many fuel cells.

As electrolysers can be ramped down they might in future be used to cope with electricity supply demand mismatch.^[34]

Efficiency

Industrial output

Efficiency of modern hydrogen generators is measured by *energy consumed per standard volume* (MJ/m^3) , of hydrogen assuming standard temperature and pressure of the H_2 . The lower the energy used by a generator, the higher its efficiency would be; a 100%-efficient electrolyser would consume kilowatt-hours kilogram 39.4 per (142 MJ/kg) (higher heating value) of hydrogen, [35] 12,749 joules per litre (12.75 MJ/m³). Practical electrolysis (using a rotating electrolyser at 15 bar



electrolysis of water, for production of hydrogen.

pressure) may consume 50 kW·h/kg (180 MJ/kg), and a further 15 kW·h (54 MJ) if the hydrogen is compressed for use in hydrogen cars.^[36] By adding external heat at 150 °C (302 °F), electricity consumption may be reduced.^[37]

Electrolyzer vendors provide efficiencies based on <u>enthalpy</u>. To assess the claimed efficiency of an electrolyzer it is important to establish how it was defined by the vendor (i.e. what enthalpy value, what current density, etc.).

There are three main technologies available on the market: **alkaline**, **solid oxide**, and **proton exchange membrane** (PEM) electrolyzers. Alkaline electrolyzers are cheaper in terms of investment (they generally use nickel catalysts), but least efficient. PEM electrolyzers are more expensive (they generally use expensive platinum-group metal catalysts) but are more efficient and can operate at higher current densities, and can, therefore, be possibly cheaper if the hydrogen production is large enough. Solid oxide electrolyzer cells (SOEC) are the third most common type of electrolysis, and use high operating temperatures to increase efficiency. The theoretical electrical efficiency of SOEC is close to 100% at 90% hydrogen production.^[38] Degradation of the system over time does not affect the efficiency of SOEC electrolyzers initially unlike PEM and alkaline electrolyzers. As the SOEC system degrades, the cell voltage increases, producing more heat in the system naturally. Due to this, less energy is required to keep the system hot, which will make up for the energy losses from dramatic degradation initially.^[39]

Conventional alkaline electrolysis has an efficiency of about 70%.^[40] Accounting for the accepted use of the <u>higher heating value</u> (because inefficiency via heat can be redirected back into the system to create the steam required by the catalyst), average working efficiencies for <u>PEM electrolysis</u> are around 80%.^{[41][42]} This is expected to increase to between 82 and 86%^[43] before 2030. Theoretical efficiency for PEM electrolysers are predicted up to 94%.^[44]

Considering the industrial production of hydrogen, and using current best processes for water

electrolysis (PEM or alkaline electrolysis) which have an effective electrical efficiency of 70-80%, [44][45][46] producing 1 kg of hydrogen (which has a specific energy of 143 MJ/kg) requires 50-55 kW·h (180-200 MJ) of electricity. At an electricity cost of 0.06/kWh, as set out in the US Department of Energy hydrogen production targets for 2015,^[47] the hydrogen cost is \$3/kg. Equipment cost depends on mass production. As of 2022, different analysts predict annual manufacture of equipment by 2030 as 47 GW, 104 GW and 180 GW, respectively.^[48]

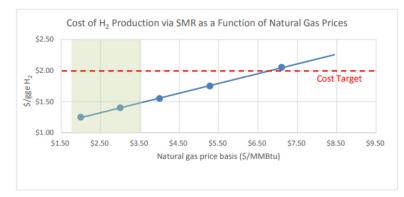


Figure 4 H₂ production cost (\$/gge untaxed) at varying natural gas prices for current DNGR technology (assuming 1,500 gge/day plant size and economy of scale in plants deployment). Cost target for hydrogen (<2.00/gge) can be met with a price of NG < 7.00 /MMBTU. The shaded area represents the range of natural gas spot prices for 2016.¹⁶

H₂ production cost (\$-gge untaxed) at varying natural gas prices

With the range of natural gas prices from 2016 as shown in the graph (Hydrogen Production Tech Team Roadmap, November 2017 (https://www.energy.gov/sites/prod/files/2017/11/f46/HPTT%20 Roadmap%20FY17%20Final_Nov%202017.pdf)) putting the cost of steam-methane-reformed (SMR) hydrogen at between \$1.20 and \$1.50, the cost price of hydrogen via electrolysis is still over double 2015 DOE hydrogen target prices. The US DOE target price for hydrogen in 2020 is \$2.30/kg, requiring an electricity cost of $0.037/kW\cdoth$, which is achievable given 2018 PPA tenders^[49] for wind and solar in many regions. This puts the \$4/gasoline gallon equivalent (gge) H₂ dispensed objective well within reach, and close to a slightly elevated natural gas production cost for SMR.

In other parts of the world, the price of SMR hydrogen is between 1-3/kg on average. This makes production of hydrogen via electrolysis cost competitive in many regions already, as outlined by Nel Hydrogen^[50] and others, including an article by the IEA^[51] examining the conditions which could lead to a competitive advantage for electrolysis. The large price increase of gas during the 2021–2022 global energy crisis made hydrogen electrolysis economic in some parts of the world.^[52]

Some large industrial electrolyzers are operating at several megawatts. As of 2022, the largest is a 150 MW alkaline facility in Ningxia, China, with a capacity up to 23,000 tonnes per year. [53] While higher-efficiency Western electrolysis equipment can cost 1,200/kW, lower-efficiency Chinese equipment can cost 300/kW, but with a lower lifetime of 60,000 hours.[54]

Overpotential

Real water electrolyzers require higher voltages for the reaction to proceed. The part that exceeds 1.23 $V^{[55]}$ is called <u>overpotential</u> or overvoltage, and represents any kind of loss and nonideality in the electrochemical process.

For a well designed cell the largest <u>overpotential</u> is the <u>reaction overpotential</u> for the four-electron oxidation of water to oxygen at the anode; <u>electrocatalysts</u> can facilitate this reaction, and <u>platinum</u> alloys are the state of the art for this oxidation. Developing a cheap, effective electrocatalyst for this reaction would be a great advance, and is a topic of current research; there are many approaches, among them a 30-year-old recipe for molybdenum sulfide, <u>[56]</u> graphene quantum dots, <u>[57]</u> carbon

<u>nanotubes</u>, [29] perovskite, [58] and nickel/nickel-oxide. [59][60] Tri-molybdenum phosphide (Mo3P) has been recently found as a promising nonprecious metal and earth-abundant candidate with outstanding catalytic properties that can be used for electrocatalytic processes. The catalytic performance of Mo3P nanoparticles is tested in the hydrogen evolution reaction (HER), indicating an onset potential of as low as 21 mV, H2 formation rate, and exchange current density of 214.7 µmol s-1 g-1 cat (at only 100 mV overpotential) and 279.07 µA cm-2, respectively, which are among the closest values yet observed to platinum. [61][62] The simpler two-electron reaction to produce hydrogen at the cathode can be electrocatalyzed with almost no overpotential by platinum, or in theory a hydrogenase enzyme. If other, less effective, materials are used for the cathode (e.g. graphite), large overpotentials will appear.

Thermodynamics

The electrolysis of water in standard conditions requires a theoretical minimum of 237 kJ of electrical energy input to dissociate each mole of water, which is the standard <u>Gibbs free energy</u> of formation of water. It also requires energy to overcome the change in entropy of the reaction. Therefore, the process cannot proceed below 286 kJ per mol if no external heat/energy is added.

Since each mole of water requires two moles of <u>electrons</u>, and given that the <u>Faraday constant</u> F represents the charge of a mole of electrons (96485 C/mol), it follows that the minimum voltage necessary for electrolysis is about 1.23 V.^[63] If electrolysis is carried out at high temperature, this voltage reduces. This effectively allows the electrolyser to operate at more than 100% electrical efficiency. In electrochemical systems this means that heat must be supplied to the reactor to sustain the reaction. In this way thermal energy can be used for part of the electrolysis energy requirement.^[64] In a similar way the required voltage can be reduced (below 1 V) if fuels (such as carbon, alcohol, biomass) are reacted with water (PEM based electrolyzer in low temperature) or oxygen ions (solid oxide electrolyte based electrolyzer in high temperature). This results in some of the fuel's energy being used to "assist" the electrolysis process and can reduce the overall cost of hydrogen produced.^[65]

However, observing the entropy component (and other losses), voltages over 1.48 V are required for the reaction to proceed at practical current densities (the thermoneutral voltage).

In the case of water electrolysis, Gibbs free energy represents the minimum *work* necessary for the reaction to proceed, and the reaction enthalpy is the amount of energy (both work and heat) that has to be provided so the reaction products are at the same temperature as the reactant (i.e. standard temperature for the values given above). Potentially, an electrolyzer operating at 1.48 V would operate isothermally at a temperature of 25° C as the electrical energy supplied would be equal to the enthalpy (heat) of water decomposition and this would require 20% more electrical energy than the minimum.

See also

- Electrocatalyst
- Electrochemistry
- Electrochemical cell
- Electrochemical engineering
- Electrolysis

- Gas cracker
- Hydrogen production
- Methane pyrolysis (for Hydrogen)
- Noryl
- Photoelectrolysis of water
- Photocatalytic water splitting
- Electrochemical reduction of carbon dioxide
- Timeline of hydrogen technologies
- Water purification

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- "Electrolysis of Water" (https://web.archive.org/web/20060314055443/http://chemmovies.unl.edu/ Chemistry/dochem/DoChem044.html). *Do Chem 044*. Archived from the original (http://chemmovi es.unl.edu/Chemistry/DoChem/DoChem044.html) on 14 March 2006. Retrieved 20 November 2005.
- EERE 2008 100 kgH2/day Trade Study (http://www.hydrogen.energy.gov/pdfs/review08/pd_11_ porter.pdf)
- NREL 2006 Electrolysis technical report (https://web.archive.org/web/20081007014438/http://w ww.nrel.gov/hydrogen/pdfs/40605.pdf)

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